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Organic Peroxides

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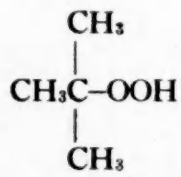
PREVIOUS to 1925, the organic chemist was restricted largely to the use of hydrogen peroxide (in concentrations up to 30%) and benzoyl peroxide for certain types of chemical reactions. In recent years, many new organic peroxides have become available and hydrogen peroxide in high purity and in greater concentration can now be obtained. The demand for new oxidizing agents has been met in part by the introduction of such compounds as acetyl peroxide, acetyl benzoyl peroxide, lauroyl peroxide, *tert.*-butylhydroperoxide, *tert.*-butyl perbenzoate, 1-hydrocyclohexyl hydroperoxide-1 and others.

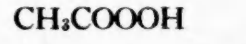
Peroxides have a special application as initiators of polymerization and consequently several compounds have been developed to satisfy the needs of the synthetic polymer industry.

In this article, a brief discussion will be given of the chemistry of organic peroxides, their usefulness in organic synthesis, in oxidation studies, for bleaching reactions, and as catalysts for polymerization, halogenation, and addition reactions.

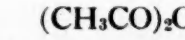
The organic peroxides may be named as derivatives of hydrogen peroxide, H–O–O–H. Hydrogen peroxide has two replaceable hydrogen atoms. If one of them is replaced by a radical, a hydroperoxide is formed. The name "peroxide" should be reserved for the compounds which have both hydrogen atoms replaced. The per-organic acids have the alternate name of the radical and hydroperoxide. Examples of this follow.



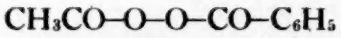
tert.-Butyl hydroperoxide



Acetyl hydroperoxide or peracetic acid

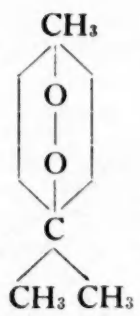


Acetyl peroxide or diacetylperoxide

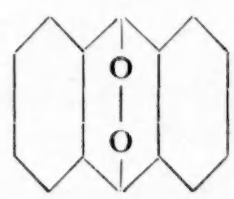


Acetyl benzoyl peroxide

Some naturally occurring peroxides have special names, for example, ascaridole, as shown below. The formation of a transannular peroxide is a typical reaction of the anthracene nucleus, as in anthracene-9, 10-peroxide.



Ascaridole



Anthracene-9, 10-peroxide

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Reagent	*Hydrogen peroxide*	*Cyclohexene hydroperoxide*
Acid potassium permanganate	Decolorized	Decolorized
Acid dichromate and ether	Blue coloration dissolves in ether	Negative—no color in ether
Ferric ferricyanide	Prussian blue formed	Prussian blue formed
Lead sulfide paper	Turns white—$PbSO_4$	Turns white—$PbSO_4$
Charcoal	O_2 liberated	Negative
Blood	O_2 liberated	Decolorization and precipitation

"Urea peroxide" is a misnomer, as it is the molar addition product of urea and hydrogen peroxide, $NH_2CONH_2 \cdot HOOH$.

The properties of these compounds are as varied as their structure. However, they will all liberate oxygen under certain conditions. They are usually determined analytically by their property of liberating iodine from acid potassium iodide solution. The iodine is then titrated with thiosulfate. The general nature of these materials may be illustrated by comparative tests on hydrogen peroxide and cyclohexene hydroperoxide tabulated as above.

It can be seen that peroxides can act both as oxidizing and reducing agents. The rapidity with which various members of this class of compounds liberate oxygen varies widely, depending chiefly on their structure. Although some peroxides are unstable and explosive, methods have been worked out for making and handling some of these compounds. Members of higher molecular weight may, with care, be handled safely. Most solutions of peroxides are quite safe since the chain reactions initiated by their decomposition are stopped by the molecules of the solvent.

Preparation

Acyl peroxides are generally prepared by starting from sodium peroxide. The preparation of p-nitrobenzoyl peroxide and perbenzoic acid is described in *Organic Syntheses*.

$$2\ p\text{–}O_2NC_6H_4COCl + Na_2O_2 \longrightarrow (p\text{–}O_2NC_6H_4COO)_2 + 2\ NaCl$$

$$(C_6H_5COO)_2 + CH_3ONa \longrightarrow C_6H_5COOONa + C_6H_5COOCH_3$$

$$C_6H_5COOONa + H_2SO_4 \longrightarrow C_6H_5COOOH + NaHSO_4$$

Methods of preparation for solutions of perbenzoic and peracetic acids in good yield have been developed as follows:

$$C_6H_5CHO + O_2 \xrightarrow[\text{ultraviolet light}]{} C_6H_5COOOH$$

$$(CH_3CO)_2O + HOOH \longrightarrow CH_3COOOH + CH_3COOH$$

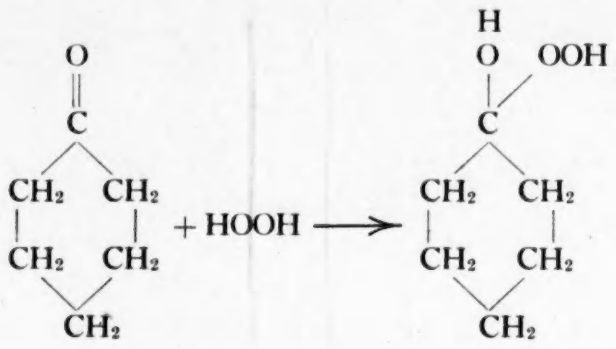
In this country, N. A. Milas has made many contributions to the methods of preparation of organic peroxides. He has found that hydrogen peroxide may be substituted for water in many reactions. Hydroperoxides are formed in a manner exactly analogous to the usual hydroxy compounds.

$$RR'R''COH + HOOH \longrightarrow RR'R''COH \cdot H_2O_2 \xrightarrow[-H_2O]{\text{Distillation}} RR'R''COOH$$

$$RCH = CH_2 + H_2SO_4 \longrightarrow RCH(OSO_3H)\text{–}CH_3$$

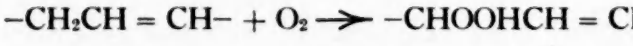
$$RCH(OSO_3H)\text{–}CH_3 \xrightarrow[\text{metal carbonate}]{HOOH} R\text{–}CH(CH_3)OOH$$

$$ROH + H_2SO_4 \longrightarrow ROSO_3H \xrightarrow[\text{metal carbonate}]{HOOH} ROOH$$



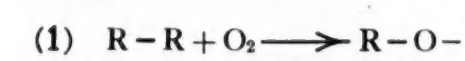
The reactions are general methods of preparation. However, the most common reaction producing peroxides is autoxidation with the molecular oxygen of air. The hydroperoxides of cyclohexene, methyl oleate, and tetralin can be obtained relatively pure. Usually, the intermediate compounds produced are not isolated but oxidation with molecular oxygen has been and will continue to be widely studied. For many years, the primary autoxidation reaction of olefins was generally assumed to be the direct addition of oxygen to the double bond.

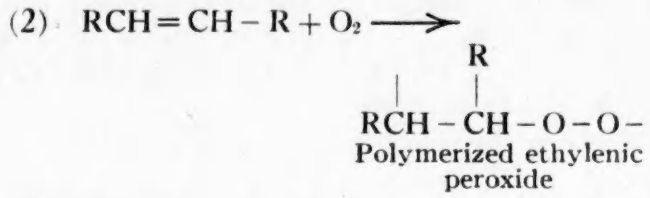
It has now been shown that in most cases of addition in unconjugated olefinic systems, molecular oxygen enters at the methylenic carbon atoms adjacent to the double bond.

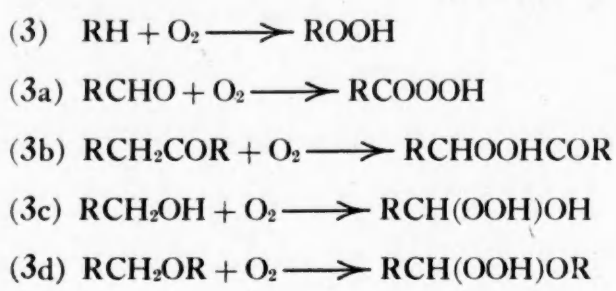


The hydroperoxide thus formed contains one atom of active oxygen and one atom of replaceable hydrogen, the double bond being left intact. This is in direct contrast to the action of ozone. Molecular oxygen usually enters between a carbon-hydrogen bond, though a carbon-carbon bond may sometimes be broken. In conjugated diolefins, additions to the unsaturated system occur in 1 and 4 positions.

Rieche summarized the addition of oxygen to organic compounds in the following set of reactions:





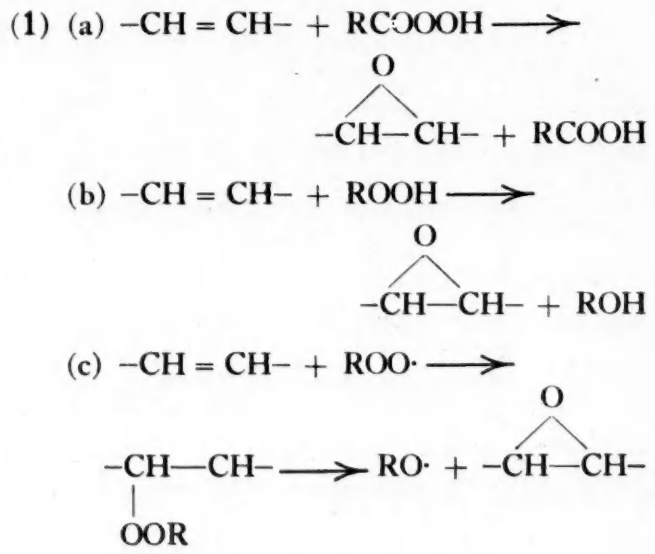


Reactions

All hydroperoxides are relatively unstable. The absorption of oxygen by organic compounds is promoted by sunlight and by numerous organic and inorganic chemical catalysts. Raising the temperature above normal appears to facilitate absorption. The decay of peroxide groups is strongly promoted by elevated temperatures, by prolonged illumination, and by certain chemical catalysts, such as iron salts, which can act both as oxidation catalysts and as peroxide destroyers. In biological systems, catalase and the peroxidases are the catalysts.

Except with the more stable peroxides, decay takes place at the same time as peroxide formation. Oxidative reactions can continue as far as chain scission. In many cases (depending on reaction conditions), a variety of intermediate products can be produced.

Farmer and coworkers summarized the reactions of peroxides as follows:



(d) $RO\cdot + -CH_2-CH=CH- \longrightarrow ROH + -\dot{C}H-CH=CH-$

(2) $-CH=CH- + ROOH \longrightarrow -CH\cdot(OR)-CH(OH)-$

(3) $-CH(O\!-\!O)-CH- \longrightarrow [-\dot{C}H(O\cdot) + -\dot{C}H(O\cdot)] \longrightarrow -CH(=O) + -CH(=O)$

(4) $-CH(OOH)-CH=CH- \xrightarrow[H_2O]{H} -CHOH-CHOH-CHOH-$

(5) $-CH(OOH)-CH=CH- \xrightarrow{RCOOH} -CH(OCOR)-CH(OCOR)-CH(OH)-$

(6) $-CH(OOH)-CR=CH- \xrightarrow[H_2O]{} HO-CH(-COR)-CH- + -COOH \longrightarrow -COOH + RCOOH + -COOH$

(7) $-CH(OOH)CH=CH \xrightarrow[\text{or heat}]{Fe} RCH(OOH)OR \longrightarrow -CO-CH=CH- + RCOOR + H_2O$

(8) $ROOH + H_2O \longrightarrow ROH + H_2O_2$

Uses

Peroxides are highly active compounds. It has been reported that the Germans used concentrated hydrogen peroxide as a source of oxygen for their rocket weapons V-1 and V-2. The drying of paints and oils is intimately tied up with peroxide formation, as is gum and varnish formation in mineral oil and gasoline. Peroxides may play an important part in biological oxidations. They afford a method of producing epoxy compounds, alcohols, aldehydes, ketones, and acids.

The decomposition of peroxides usually involves the formation of free radicals. Such radicals are exceedingly active and in general initiate chain reactions. It is this fact that has brought about their extensive use in the polymer industry. Peroxides for this reason have the ability to produce abnormal additions of reagents such as HBr, mercaptans, and bisulfites, to unsaturated compounds.

The peroxides act as catalysts in halogenation reactions and in reactions where sulfuryl chloride is used as a chlorinating and sulfonating reagent. Their use affords a method of forming acid chlorides directly from hydrocarbons and oxalyl chloride, or phosgene. Kharasch and coworkers have recently reported good yields in the reactions shown below. They open a new field in aliphatic chemistry.

$$RCH=CH_2 + CCl_4 \xrightarrow[\Delta]{(RCO)_2O_2} RCHClCH_2CCl_3$$

$$RCH=CH_2 + CHCl_3 \xrightarrow[\Delta]{(RCO)_2O_2} RCH_2CH_2CCl_3$$

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Erratum

Vol. 17, No. 2, p. 2 (1945)

In the article "Laboratory Preparation of Alkyl Amines" by Dr. J. B. Dickey, in the second equation under Section IE (2) "β-Naphthol" should have read "α-Naphthol."